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MONTHLY PROGRESS REPORTS  
Period Covered  
April 1 - 30, 1980

Date Issued: May 15, 1980

2022187100A

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MONTHLY PROGRESS REPORTS

Period Covered  
April 1 - 30, 1980

2022187100

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2022187101

Charge Number: Various  
Program Title: Analytical Research  
Written By: W. R. Harvey, R. E. Davis, D. C. Watson and J. O. Lephardt

I. HPLC Separations of Oriental Tobacco

HPLC separations of oriental tobacco has continued on a cooperative basis with the Flavor Group. Cumulative collections of three peaks detected by refractive index are in progress. These cuts will be submitted for identification by NMR and possibly mass spectrometry.

II. Side Stream/Main Stream FTC Tar Ratios

Work continues toward generation of a revised correlation for FTC tar by the acridine orange fluorescence method versus the gravimetric FTC tar method. The March 1980 CI smoke extracts used for nicotine and water determinations is being examined. This data should be complete by the end of April.

III. Tipping Paper ink/adhesive Problem

Identification of constituents extracted from the printed paper continue. Several known compounds have been received and checked for HPLC retention time. These retention times check with identification made by mass spectrometry (i.e., triphenyl phosphate). An unknown peak collected from Schweitzer-Hermetite remains unidentified.

The nitrocellulose fraction separated from the printed inks is undergoing GPC analysis by M. Logue to supply molecular weight distribution information and possibly elements so far undetected. A comparison is being made of Schweitzer-Milprint, Schweitzer-Hermetite and Ecusta 701.

The feasibility of an experimental manufacturing run using tipping paper printed with solvent systems representing variation from low to high viscosity and variations from fast to slow solvent systems is being explored in cooperation with manufacturing personnel.

IV. "Aging" of Standards for the Kjeldahl Nitrogen Method

Initial studies show that the "aging" effect (i.e., increased absorbance and scatter with age) can be eliminated by storage of the standards in Nalgene<sup>R</sup> bottles instead of the usual glass containers. The precise cause for this is not known but more studies are planned for confirmation of this important phenomenon.

2022187102

V. Puff-by-Puff Analyses by Turnable Diode Laser (TDL)

A high efficiency vacuum pump is being installed to allow puff-by-puff analyses using the 100-meter gas cell with the TDL. Four different smoking assembly designs have been evaluated for application to the unit. Since dead volume in the system affects the puff profile shape, any system used must be characterized so that valid comparisons can be made between different cigarette types.

VI. Chemometrics

The headspace collection and gc analysis has been completed for the 12 Trinity model's filler ( 6 x 85 mm and 6 x 100 mm). The chromatograms have been collated and are ready for application of chemometric techniques. Data will be generated for Cambridge to allow an over-all comparison of the headspace filler volatiles of: Kent III, Cambridge, Carlton (1 mg) and Carlton 100's.

VII. Assistance to PM International

A system for the automated determination of TPM, H<sub>2</sub>O, nicotine, and tar was installed in PM facilities in Buenos Aires, Argentina. A similar, but up-dated, system will be set-up in the Maracay, Venezuela labs during May and a 5th such unit is scheduled for Quito, Ecuador.

VIII. Study of Tobacco Constituents by FT-IR-EGA


Work is continuing on the program to identify the gaseous decomposition products of tobacco constituents. Amino acids, pectin and cellobiose are currently being examined. Tobacco cell wall material obtained from Gordon Bokelman will also be included in this study. An examination of lignin has been completed and an internal special report issued (Ac. #80-074).

*W. R. Harvey*

2022187103

CHARGE NUMBER: Various  
PROGRAM TITLE: Flavor Development  
PROJECT LEADER: C. N. Kounnas  
PERIOD COVERED: April 1 - April 30, 1980  
DATE OF REPORT: May 8, 1980

An annual report was issued during this reporting period.

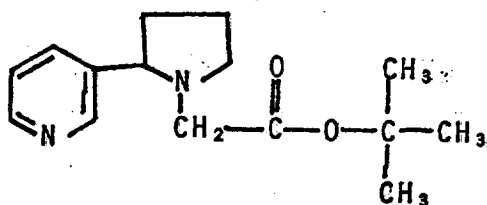


C. N. Kounnas

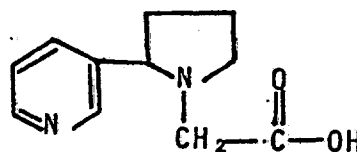
2022187104

CHARGE NUMBER: 0108  
PROGRAM TITLE: Mechanism for Smoke Formation  
PERIOD COVERED: April 1 - May 1, 1980  
PROJECT LEADER: R. A. Kornfeld  
DATE OF REPORT: May 6, 1980

The pyrolytic yields of nicotine and myosmine were calculated at several temperatures for the thermolysis of t-butyl 2-(3-pyridyl)pyrrolidinylacetate (A) and 2-(3-pyridyl)pyrrolidinyl acetic acid (B). Both of these compounds were synthesized by G. Chan as potential nicotine release agents. Preliminary information for the pyrolysis of these two compounds was reported last month.



A



B

The molar percent yields of both nicotine and myosmine from the t-butyl ester (A) were low. Up to 500°C nicotine was produced at the 0.2-0.3% level while myosmine yields were 4-5%. At 550°C the nicotine and myosmine yields were 1% and 15% respectively. The formation of nicotine and myosmine from the acid (B) are shown below. The molar percent yields of nicotine remain essentially constant until about 500°C. At temperatures above 500°C, the yield decreases. While myosmine does not produce a detectable peak until 400°C, this compound's yield increases dramatically until it approaches the amount of nicotine present.

2022187105

Temperature (°C)	Pyrolytic Molar Nicotine	Yield from B of Myosmine~
250	12%	N.D.
300	13%	N.D.
350	13%	N.D.
400	13%	5%
450	13%	12%
500	18%	16%
550	8%	6%
600	1%	3%

N.D. = not detected

Reasons for the low nicotine and relatively high myosmine yields are being pursued!

In addition to the installation of the capillary inlet system reported last month, the Hewlett-Packard gas chromatograph can now operate in a sample split or splitless mode. Several test flavor mixtures, smoke samples, and fractions of a Browning reaction mixture (in cooperation with M. Edmonds) were chromatographed.<sup>2</sup>

Several furan derivatives (2-furfural, 2-furoic acid and 5-hydroxymethyl 2-furfural) were pyrolyzed alone and copyrolyzed with ammonium carbonate at 600°C and 800°C. Based solely on GC retention data, several pyridines were tentatively identified. The only furan compound to show even a trace of pyrazines at 600°C is 2-furoic acid. All co-pyrolyzates show a trace of methyl pyrazine at 800°C. None of these co-pyrolyses produced significant amounts of simple pyrazines. Copyrolyses with another nitrogen source, glycine or alanine, will be pursued during the next month.<sup>3</sup>

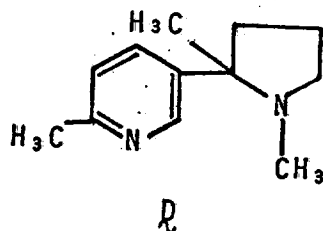
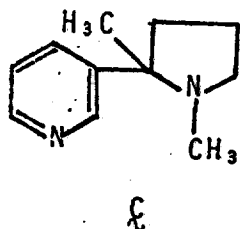
It was found that cigarettes wrapped with paper containing added phosphate yielded 50% more CO when compared to the same cigarettes using untreated or citrate treated paper.<sup>4</sup> In an attempt to determine if this observation could be explained via a pyrolysis mechanism; phosphate treated, citrate treated, and untreated cigarette papers were pyrolyzed at 800°C and the amount of CO was quantitated by gas chromatography. It was found that the untreated and treated papers yielded the same amount of CO. However, a comparison with the citrate treated (Monitor) paper showed a 15% decrease in CO yield!

A mixture<sup>5</sup> of 2<sup>1</sup>-methyl-nicotine (C) and 2<sup>1</sup>,6-dimethylnicotine (D) was analyzed by computerized GC/MS. The mass spectra were consistent with the proposed structure.<sup>6</sup>

2022187106



May 6, 1980



Pyrolysis/GC/MS analyses for the materials evaluation program continue. The following memoranda were issued:

"Pyrolysis GC/MS of Samples Z9ZF-A&C", memo to Mr. R. D. Carpenter from D. F. Magin, April 17, 1980

"Pyrolysis GC/MS of Sample Z9YW", memo to Mr. R. D. Carpenter from D. F. Magin, May 1, 1980.

References:

1. L. Brown 7223
2. F. Greene 7336
3. J. Kang 7262
4. R. Newman 6549 (Project 2501)
5. H. Secor sample number 7386-149C
6. D. Magin 7474

*Rich Kornfeld*

/iw

2022187107

CHARGE NUMBER: 0307  
PROJECT TITLE: Cigarette and Tobacco Measurement Methods  
PROJECT LEADER: C. L. Irving  
PERIOD COVERED: April, 1980  
DATE OF REPORT: May 7, 1980

I. Moisture Measurement

The dual channel Instrument Interface Controller (IIC), which was received from Engineering Services last month, was used to collect a single channel of data from the microwave oven being built by Engineering Services. No problems were encountered with the unit in this test. In addition, software was written to transform the data into a form suitable for input into available regression routines. Further tests are planned to simulate two channel data input.

Work on the automatic microwave moisture meter at Steinbrecher Corporation is proceeding on schedule. The X-band sampling head has been assembled and we have supplied the quartz tubes necessary for the unit so that final check-out of the head can begin. The L-band sampling head is currently being assembled. Tobacco samples at three moisture levels were supplied to Dr. Steinbrecher so that final cavity dimensions for the L-band unit can be determined along with the optimum location for the sample in the cavity to achieve maximum system response. The entire moisture meter is now expected to be shipped about the 1st of June, 1980.

The Motorola MA-5 Moisture Analyzer, an improved version of the original Computrac Moisture Analyzer, was evaluated. This unit has an improved balance and can be set to any temperature between 65 and 175°C. The unit was evaluated with ET, DET, RL, and bright tobaccos, with and without the flavors they would have in a Marlboro, and with Marlboro and Merit blends. The tests showed the unit to give moisture readings with approximately the same error as the OV test. The difference between Motorola readings and OV results were found to be a function of tobacco type and oven temperature but not of tobacco moisture. By choosing the operating temperature of the Motorola unit correctly the difference between Motorola and OV results could be reduced to  $0.30 \pm 0.5$  OV units for all tobaccos tested except ET, for which the difference was  $-0.10$  OV units. These results indicate the Motorola unit could be used to predict OV to an accuracy of  $\pm 1.0$  OV units at a 95% confidence level. The time required to obtain moisture values from the Motorola unit was  $13.6 \pm 5.2$  minutes. Due to the poor accuracy of the Motorola unit and the length of time required to obtain a reading the unit will be returned to the manufacturer.

2022187108

## II. Cylinder Volume Testing

Using the math modeling programs and the daily OV monitor data from the Materials Evaluation Facility the variation that can be expected in equilibrated CV results of ET and DET from RH variations (within control limits) was determined. The OV monitor data from September, 1979 through January, 1980 was averaged and the model was used to predict an RH range from the OV range (mean  $\pm 2\sigma$ ) of the monitor. This RH range was used to calculate a CV range of  $\pm 2.9$  cc/10g for both ET and DET due to RH variation alone. Knowing the variation of CV values that can be expected from variations in laboratory conditions should help in the evaluation of data of expanded tobaccos.

An experiment, designed by Mr. J. Tindall, was run to determine the effect of operators on CV test results. This test, using uncased bright tobacco, showed the difference between operators to be as high as 1.2 cc/10g. The test also showed an average difference of 1.0 cc/10g between Rooms D-105 and D-112. This difference between rooms was also found to change from day to day. While this experiment does indicate statistically significant differences exist between operators, laboratories, and days, the differences are small and should present no problems in interpreting results from properly designed experiments.

*Christopher L. Lving*

mkb

2022187103

CHARGE NUMBER: 1005  
PROJECT TITLE: Improved Semiworks Operations  
PROJECT LEADER: J. F. Sherwood  
PERIOD COVERED: April, 1980  
DATE OF REPORT: May 8, 1980

I. Primary Processing

A. WS Application

An MSA combustible gas indicator calibrated for ethanol was purchased and used to measure the concentrations of ethanol in air in and around the equipment used to apply WS to tobacco in the Pilot Primary. The measurements showed that ethanol concentrations in the after-cut cylinder can exceed 60% of the lower explosive limit (LEL) when WS/ethanol solutions are applied to tobacco. According to Manufacturing guidelines an explosion suppression system must be used in equipment where the possibility of exceeding 60% of the LEL exists. Therefore, plans are to install a Fenwal explosion suppression system, similar to those used in Manufacturing, on the after-cut cylinder in the Pilot Primary.

Also, two modifications were made to the equipment to improve safety during after-cut spraying. The blade in the cylinder exhaust fan was replaced with a nonsparking aluminum blade and additional exhaust was added to the cylinder discharge hood to reduce ethanol concentrations both in the hood and on the cylinder discharge conveyor.

B. Cut Width Study

A study to investigate the effect of cut width, ranging from 20-60 cuts/in, on blend and cigarette properties is in progress. Sieve, CV/OV, and maker efficiency data have been collected and forwarded to Mr. J. E. Tindall for analysis. Analytical and compacimetric firmness testing of cigarettes produced in this test is in progress.

II. Cigarette Making and Packing

A. High Speed Seam Sealing

The Kaymich adhesive application system used with the National 25-1088 PVA liquid side seam adhesive was installed for evaluation on a Mark 9-5 maker (4A7) in the MC on April 30, 1980. Both the applicator and the adhesive appear to be functioning well and MC QA personnel are monitoring the quality of the cigarettes produced in this evaluation.

Marlboro and Merit cigarettes for two POL tests (N-3121 and N-4139) of the Polymer Industries 428-156-1 PVA liquid side seam adhesive passed subjective testing by the Flavor Development group as well as analytical testing, and were released for shipment.

2022187110

B. Pneumatic Feeder Evaluation

A test run at the request of Manufacturing to evaluate the firmness characteristics of Marlboro cigarettes made with tobacco conveyed by two pneumatic feeders under evaluation in the MC, one made by Hauni and the other by Cardwell, was completed. In the first part of the test, the Hauni feeder supplied the first four makers in line 2A and the Cardwell system the second four. In the second part of the test, the feeders were switched to avoid any maker effects.

The results showed no evidence of any significant differences in the equilibrium firmness levels of the cigarettes produced with tobacco conveyed by the two feeders.

  
J. F. Sherwood

mkb

2022187111

CHARGE NUMBER: 1101  
PROGRAM TITLE: ENTOMOLOGICAL RESEARCH  
PERIOD COVERED: April 1-30, 1980  
PROJECT LEADER: M. A. Manzelli  
DATE OF REPORT: May 6, 1980

I. INSECT GROWTH REGULATOR

A. Stemmary Application to Burley

Of the 220 burley KABAT® treated samples that were analyzed, 183, or 83%, fell within the 10 ppm  $\pm$  2 ppm residue target range. The residue spread was 7-16 ppm, and the average for all analyses was 10.4 ppm of methoprene.<sup>1</sup>

B. Maury Street Warehouse KABAT® Study

This study, which has as its objective to monitor the cigarette beetle population developing in four warehouses filled only with KABAT® treated strips has been initiated. It involves the following warehouses: 14, 20, 24, and 28 as KABAT® holdings, and 15, 19, 21, 26, and 29 as nonKABAT® controls. Various combinations of DDVP/PH<sub>3</sub>/no pesticide treatments are involved.

C. Miniwarehouse Test

A repeat of the miniwarehouse study of 1978-1979 is underway. The test parameters are identical to that of the previous one, except that in this instance any infestation will not have been artificially induced.<sup>2</sup>

D. Commercial Application of KABAT®

The responsibility for initiating KABAT® application on a regular basis in PM and Universal Leaf stemmeries has been delegated to Mr. W. Floyd Johnson of Leaf.

II. PHYSIOLOGY OF THE CIGARETTE BEETLE

One replicate of nonacclimated exposure of insects to a temperature of -6.7°C has been completed, and a second one initiated. Data collections have not been completed.

III. REFERENCES

1. Lehman, R. M. Notebook No. 7235, p. 73.
2. Lehman, R. M. Notebook No. 7235, p. 72.

nwp

*M.A. Manzelli*

2022187112

CHARGE NUMBER: 1307  
PROGRAM TITLE: Reconstituted Tobacco Development  
PERIOD COVERED: April 10 - 30, 1980  
PROJECT LEADER: G. Gellatly

## I. RL PROCESS

The search for equipment to coat a homogenized mixture of STP and CEL on RL base web continued. Coating equipment in the laboratories of AER and St. Regis Corporations was judged to exert too great a strain on the sheet.<sup>1</sup> Another type of coater was recommended by these companies (zero angle blade coater) which will be evaluated in the laboratories of Black Clawson Corporation.

The rate of evaporation fouling by the extract liquor of the burley fraction (66% burley stems, 34% burley by-products) of the RL blend was found to be no greater than the whole blend<sup>2</sup> (34% burley stem, 32% bright stems, 34% mixed STP). This trial was made to determine if separate burley processing, which increases the degree of RL denitration, would present a processing problem in Park 500. However, an RL blend change has since been made which necessitates repeating this fouling rate comparison (90% burley stems in the burley fraction of the blend). The higher burley stem content is expected to increase significantly the rate of evaporator fouling.

## II. RL PRODUCT

A cost estimate of \$140,000 was established for the installation of a tunnel dryer in the RL Pilot Plant to make a direct filling power comparison with Yankee drying. Preliminary experiments showed that a 10% increase in filling power can be achieved. However, the request for authorization of funds<sup>3</sup> will be delayed until dielectric and microwave drying of sheet has been evaluated.<sup>4</sup>

A program was initiated to darken the color of RL sheet to that of cased burley strip. The objective is to achieve this darker color by use of less than ~2% additive.

## III. DENITRATION

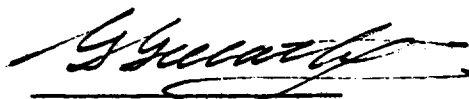
The maximum flow and concentration of the RL extract liquor to be treated in the second generation denitration process was determined to be 80 gpm of 11% HWS and 2500 ppm  $\text{NO}_3\text{-N}$ . Both the electrodialysis and the anaerobic processes can effect denitration of this liquor but the aerobic process requires the HWS content to be reduced by dilution to 8% HWS. Using the split flow mode of operation which reduces the volume to be treated to 48 gpm, the liquor concentration is increased to a maximum of 18% HWS and 3,000 ppm  $\text{NO}_3\text{-N}$ . Only the electrodialysis process has reliably demonstrated denitration of this concentration liquor. The development of the aerobic process to denitrate liquor of this higher concentration is proceeding. Comparison of the smoke chemistry of cigarettes containing RL denitrated by electrodialysis, anaerobic and aerobic fermentation indicates significantly higher levels of phenols, catechols and HCN deliveries of the cigarettes containing sheet denitrated by the aerobic fermentation process (FTR).<sup>5</sup> The economic evaluation of these second generation processes continues.

2022187113

Development work is being intensified to find a practical process for disposal of the brine from the electrodialysis process. Concentration of the brine from 8% to 30% TS before crystallization yields a cleaner looking product than the present potassium nitrate product of Park 500. Other means of brine disposal being considered are brine exchange before or after crystallization for extract liquor from Lines 1 and 2, using the chilled brine for wash liquor for first stage centrifuge sludge on Lines 1 and 2 and solvent extraction.

#### IV. REFERENCES

- <sup>1</sup> Memo "Investigation of Coating Equipment at AER and St. Regis Corporations" to G. Gellatly from R. O. Ellis, 4/24/80.
- <sup>2</sup> RL Pilot Plant Test File #577.
- <sup>3</sup> Engineering Cost Estimate re RL Tunnel Dryer Installation, Job #1918Ac.
- <sup>4</sup> Memo "Use of Dielectrics for Improved Drying and Increased Filling Power of RL Sheet" to G. Gellatly from R. Z. de la Burde and R. O. Ellis, 4/23/80.
- <sup>5</sup> Minutes of a meeting to discuss 2nd generation RL DN processes, 4/24/80.



G. Gellatly

/jb

2022187114



CHARGE NUMBER: 1503  
PROGRAM TITLE: Modified Smoking Materials  
PERIOD COVERED: April 1 - 30, 1980  
PROJECT LEADER: G. D. Keritsis

## I. GAS PHASE CONTROL

The silica gel-permanganate based granular filter material was found to remove 45% of NO from smoke after five weeks of aging in cigarettes at room temperature. Such aging tests will be continued to determine the causes that deactivate the filter material. A titration method has also been developed for ascertaining the amounts of  $\text{MnO}_4^-$  and  $\text{MnO}_2$  on the granular filter material. This will permit correlation of loss of gas phase activity upon storage with the amount of residual  $\text{MnO}_4^-$  and will also permit investigation of the stoichiometry and mechanism of the interaction of NO with  $\text{MnO}_4^-$ .<sup>1</sup>

Cigarette candidates containing fillers of varying cut widths and chemical compositions (from salt casing) will soon be submitted for smoking.<sup>2</sup>

## II. RECONSTITUTED TOBACCO

Several denitration runs of Park 500 SEL/CEL combinations were made using the ED process in an effort to generate additional data needed for the economic evaluation comparison with other denitration processes.<sup>3</sup> Satisfactory runs were also made by Project 1307 personnel using the pilot plant ED unit.

An effort was made to develop technology for treating the ED brine and produce a purer  $\text{KNO}_3$  by-product while recovering desirable tobacco solubles for reapplication. The initial feasibility study indicates that the crystallization process could be applied to the concentrated ED brine (>30% solids) to recover about 60% of low in nitrate brine solubles while producing a purer  $\text{KNO}_3$  crystalline material.<sup>4</sup> The low in nitrate brine solubles could then be returned to the extensively denitrated tobacco solubles for reapplication onto the extracted tobacco. Project 1307 personnel are now scaling up this process using pilot plant equipment and quantities for a better material balance.

The initial feasibility study of recovering denitrated burley stem wash solubles for reapplication in RCB has shown no adverse effects on the RCB subjectives, chemistry of smoke and filling capacity by comparison to the standard RCB that does not utilize the burley stem wash solubles.<sup>5</sup> For this study the burley stem wash solubles were concentrated and denitrated using the ED process. A recommendation was made to repeat the feasibility study using the optimized versions of ED and anaerobic fermentation for maximum reduction of such gas phase smoke components as NO, HCN and CO.

An effort is being made to find conditions that will allow processing of stem-free tobacco dust into RCB sheet with/without the use of binder additives.<sup>6</sup>

It has been found possible to crimp RL sheet between intermeshing gears and set the crimp with a peroxide spray followed by heat treatment. The shredded material displayed about a 15% increase in CV regardless of the direction of shredding with respect to the direction of the crimps.<sup>7</sup>

2022187115

### III. REFERENCES

- <sup>1</sup> Notebook 7278, p. 139, N. B. Rainer.
- <sup>2</sup> Notebook 7395, pp. 50, 51, 59-63, 65, 66, J. W. Leik.
- <sup>3</sup> Notebook 7347, pp. 125-144, H. A. Jones.
- <sup>4</sup> Memo "Treatment of ED Brine" to K. S. Burns from G. D. Keritsis, 5/6/80.
- <sup>5</sup> Memo "Burley Stem Wash Denitration/Reapplication in RCB" to K. S. Burns from S. G. Muller, 3/7/80.
- <sup>6</sup> Notebook 7395, pp. 54-58, 64, J. W. Leik.
- <sup>7</sup> Notebook 7278, p. 139, N. B. Rainer.



G. D. Keritsis

/jb

2022187116

CHARGE NUMBER: 1600  
PROJECT TITLE: Smoker Psychology  
PERIOD COVERED: April 1-30, 1980  
PROJECT LEADER: W. L. Dunn  
DATE OF REPORT: May 12, 1980

Project Title: Annual Monitoring of Cigarette Acceptability (Year 4)  
Written by: F. J. Ryan

Ballots have been received from 2972 panelists, and coding will be completed by May 15. Results will be in the next monthly report.

Project Title: Salivation Response to Merit Regular, Merit Menthol, and Merit Regular Plus WS  
Written by: F. J. Ryan

Excreted saliva before, during, and after smoking or dry-puffing these three cigarettes is being measured. Data are complete for 9 smokers, 5 more are being tested, and 2 more are sought. Data gathering should be completed this month.

Project Title: Nicotine Discrimination at Marlboro Delivery  
Written by: F. J. Ryan

Testing has begun to see whether R&D smokers can discriminate between nicotine deliveries at Marlboro level. Twenty smokers will each make 20 comparisons. Seven have begun testing.

Project Title: Acceptability of Differential Nicotine Deliveries at 6 mg Tar  
Written by: F. J. Ryan

The first test samples made proved too low in FTC tar, are being remade.

Project Title: Cigarette Firmness Discrimination  
Written by: F. J. Ryan

In response to a request from Chris Irving, a series of tests of smoker response to cigarettes of different firmness is now being designed to help support Project 0307.

We are interested (1) in whether smokers can detect firmness differences in unlit and lit cigarettes, (2) in how their judgments compare to machine judgments, and (3) in how firmness affects acceptability ratings during smoking and snuffout.

2022187117

Project Title: Equipment  
Written by: F. P. Gullotta

The Nova 4S was installed. Its current capabilities are those of the Nova 2 (as of 4/17).

Project Title: Spectral Analysis of EEG Data  
Written by: F. P. Gullotta

S. Osborne has begun to devise a program to give power spectral density functions for EEG data. Several experiments await analysis.

Project Title: Auditory Evoked Potentials  
Written by: F. P. Gullotta

We have previously demonstrated that cigarette smoking and abstention have no effect on auditory evoked potentials to pure tone stimulation. We are presently running a group of nonsmokers to ascertain whether their EPs can be differentiated from those of smokers.

Project Title: The Discriminative Stimulus Properties of  $\ell$ -nicotine and Nicotine Analogues  
Written by: V. J. DeNoble

A series of studies have begun that will evaluate the effectiveness of  $d\ell$ -3 methylethylaminomethylpyridine,  $d\ell$ -diethylaminomethylpyridine, 2-Isonicotine and 4-Isonicotine in producing nicotine-like interoceptive responses in rats. In addition we are collecting data to form dose response curves generated from injection of  $\ell$ -nicotine and nicotine analogues.

Project Title: The Effects of Intraventricular Injections of  $\ell$ -nicotine and Nicotine Analogues on Activity and Schedule-Controlled Behavior  
Written by V. J. DeNoble

Intraventricular injections of  $\ell$ -nicotine have been shown to produce a prostration syndrome that appears to be specific to nicotine-cholinergic activity. We are using two methods to investigate this phenomenon. (1) behavior rating scales and (2) operant behavior. The rating scale has proven successful to screen nicotine analogues for gross behavioral and central nervous system effects. The schedule-controlled behavior tests are in the baseline data collection phase.

Project Title: Self-Administration of  $\ell$ -nicotine: the Effects of Fixed Ratio Size and Dose  
Written by: V. J. DeNoble

At present the equipment is being set up for this project. It is expected that initial testing will begin with 30 days.

2022187118

Project Title: Unobtrusive Monitoring of Inhalation  
Written by: J. A. Jones

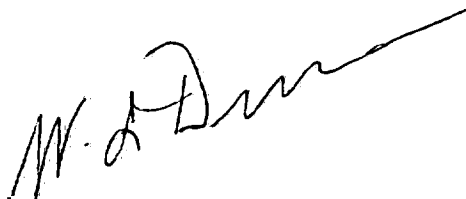
Five smokers have participated in a three-day pilot study examining alteration in inhalation pattern as a function of delivery of cigarette smoked. Immediately evident are the individual differences in inhalation patterns for a given cigarette. Some smokers demonstrate a deep inhalation followed by immediate exhalation, whereas other individuals tend to inhale a smaller volume but retain the smoke-laden inhalation for a period of seconds before exhaling. The MINC computer to be used in future studies will permit analysis of the parameters of inhalation volume, duration or retention time and, therefore, smoke exposure.

System accuracy following calibration continued to be very acceptable, on the order of .90 and above for a range of respiration volumes.

The mobile apparatus is en route to Philip Morris and should arrive within the next two weeks.

Project Title: Ultra-Low Delivery Smokers' Study  
Written by: S. R. Dunn

A research proposal has been completed and should be available for dissemination shortly. The study will be focused on 45 year-old, white, female professionals. Data collection will be by a structured face to face interview method. The interview procedures are currently being tested and refined with in-house participants. Subject recruitment through the Virginia Panel is underway.



2022187119

PROJECT CHARGE: 1702

PROJECT TITLE: FILTRATION PHYSICS

PROJECT LEADER: R. W. Dwyer

PERIOD COVERED: April 1-30, 1980

DATE OF REPORT: May 8, 1980

## I. FILTER DESIGN

### A. FILTER EFFICIENCY (1,2)

The flow rate range of our filtration efficiency study has been extended down to 100 cc/min. The efficiencies of MM20 rods and filters have now been measured from 100 to 1000 cc/min. Additional filters at a variety of RTD's have been obtained in order to isolate the effect of this variable on efficiency.

### B. DESIGN MODELLING (1)

The delivery model is being used to predict puff-by-puff TPM deliveries for a variety of filter designs. In conjunction with the New Product Development Project, we are designing potential filters for a dual-stage filter candidate. Several designs are predicted to deliver more TPM on the initial puffs than a conventional single-stage filter at the same total delivery level.

### C. NOVEL FILTER DESIGNS

Based on the results of FTC tar measurements, hollow-tipped cigarettes and conventional controls are being hand constructed and diluted. These 5 mg candidates will be submitted to SEF for evaluation.

In order to assess the effects of aerosol particle size on subjective impact, Merit 85's are being modified with partial filter by-pass channels. This filter design has been shown to give rise to larger smoke particles. These cigarettes will be constructed to give equivalent TPM deliveries as regular Merits and then smoked for subjective evaluation.

## II. AEROSOL CONTROL

### A. FILTRATION EFFECTS (4)

A study of the filtration efficiency of tobacco rods as functions of both particle size and particle velocity is in progress. Preliminary results with pressure drop selected rods show that in the flow range of 200 to 2000 cc/min the filtration efficiency exhibits a minimum. This occurs at about 1000 cc/min for 60 mm rod lengths.

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B. COMPOSITION AND GROWTH (5)

Over thirty scattering patterns for MM20 smoke particles coagulated for one minute at 80% relative humidity have been analyzed. The refractive index calculated from the scattering patterns varied from 1.43 to 1.61 and showed no correlation with particle size. Experiments are now in progress to determine the refractive index of particles from uncoagulated fresh smoke.

REFERENCES

- 1) R. W. Dwyer, Notebook 7327.
- 2) S. G. Abel, Notebook 7303.
- 3) M. L. Fleming, Notebook 7342.
- 4) R. M. Creamer, Notebook 7237.
- 5) D. D. McRae, Notebook 7330.

/ev

RWDwyer

2022187121

PROJECT CHARGE: 1703

PROJECT TITLE: FILTRATION CHEMISTRY

PROJECT LEADER: C. B. Hoelzel

PERIOD COVERED: April 1-30, 1980

DATE OF REPORT: May 8, 1980

#### ADHESIVE TESTING (T. V. Van Auken)

The Max S-based adhesive tester continues to be a popular item. This month tests have been run for QA (National 3759-1-1 vs Ajax 563-8) and Louisville (Fuller 3934 vs Ajax 563-8 and 563-6). A study has also been done on Ajax 563-6, 563-8 and 3563. This last adhesive is of particular interest because of the high degree of thixotropy it exhibits.

A memo has been written outlining the various factors which we presently envision checking with the Max S-based adhesive tester, and in detail how each factor is to be tested.

The motor change and installation of a 2:1 right angle gear drive has solved most of the tester's problems. Two significant problems, and one minor one remain. (1) The axes of the two rollers are not quite parallel. To correct this would require a complete redesign of the unit. In view of the fact that Mark II is in the design stage, it is probably not worth rebuilding the Mark I version. (2) The nip pressure is unknown, and probably not reproducible. This can be corrected with a relatively minor redesign, but we first need to know what the nip pressure in the tippers actually is. (3) Presently it is difficult to make appropriate changes in the motor speed because of the coarse response of the controller "pot". A new 10-turn pot will be installed soon.

A visit to Hauni Richmond, and a long discussion with Sigfred Abrahams produced a list of Hauni parts probably needed for the Mark II tester. These materials have been turned over to Ed Moss, who is designing the mechanics of the Mark II.

#### ADHESIVES TECHNOLOGY (T. V. Van Auken and C. B. Hoelzel)

A combined trip to Findley Adhesives and to Milprint, both in Milwaukee, Wisconsin, was made. At Findley we heard presentations on latex and hot melt adhesives. At Milprint Lee Brazier discussed his ideas and plans for developing and applying a pre-applied adhesive for tipping paper.

A vertical column, about seven feet high, has been assembled for the purpose of studying settling of adhesives during storage. The column has sample taps at ca sixteen inch intervals so that size distribution profiles can be obtained as a function of depth and time.

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ADHESIVE PROBLEMS (M. Logue, A. Robinson and C. B. Hoelzel)

The data collected from the Stockton Street study concerning the curing time of Carbowax 750 was reviewed. There was a change in curing time as machine temperature and ambient conditions changed. The firmness gage was not working properly at the time of testing; therefore, no conclusions can be made about the firmness of the tow.

A second test will be conducted beginning May 19, 1980. At this time the temperatures on Machine #21 will be controlled and areas of heat loss will be insulated. The objective of this test will be to find the optimum machine operating conditions which will produce a consistently acceptable charcoal plug in a minimum amount of time.

During the month, two problems arose in the Manufacturing Center which were attributed to the tipping adhesive. In the first case, Ajax 563-8 became discolored (yellowish) and coagulated on a PA-8 tipper (4A5). A sample of the adhesive was obtained to determine the cause of discoloration.

The adhesive from the machine was washed (in a Soxhlet Extraction Apparatus) with acetone and distilled water. The washed adhesive residue retained a yellowish-gold color. This color and the appearance of the residue suggested the discoloration was caused by cork-paper contamination. To evaluate the cause of the adhesive discoloration, bits of Ecusta 3207 cork-tipping paper were blended in a Waring Blendor with a fresh sample of Ajax 563-8 adhesive. Within a few minutes after blending had begun, the adhesive sample began to turn yellow. The degree of yellowing depended on how long the adhesive and paper were blended together.

This discoloration could conceivably happen on the PA-8 by a piece of cork-paper being mechanically worked in the adhesive on the pickup roller and/or between the roller housing.

As additional evidence to support the cause of the adhesive discoloration, M. E. Counts of the Biomaterial Division examined the washed adhesive residue by scanning electron microscopy (30X). The gold regions of the residue appeared fibrous in character. This type of fibrous structure is characteristic of paper when viewed microscopically.

In the second case, the undercut applicator roll from a PA-8 tipper (3C4) was etched to the point that portions of the lands were entirely removed. With the aid of Bill Carter, we examined the roll under high magnification. The condition of the roll and the manner in which it was etched indicates that the "etching" was the result of high pressure rolling contact between the two rollers in the applicator. This could have come about because the tension was set too high and may have been exaggerated by running in contact without any adhesive in the nip.

MENTHOL TRANSFER (T. E. Majewski)

The menthol migration/ageing study using mentholated cigarettes with

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varying amounts of triacetin in the cellulose acetate filter is in progress. Packaged cigarettes as well as cigarettes stored in sealed cans are being analyzed periodically for menthol migration and puff-by-puff delivery.

A week was spent in attendance at a Hewlett-Packard Chromatography Course.

MISCELLANEOUS STUDIES (M. Logue)

The hexane insoluble polymers from printed tipping paper were analyzed by GPC for Bob Armstrong. The three samples were very similar using both a refractive index and a UV detector. Four Polymers were present. The information was reported in a memo to Armstrong.

CB Hoelzel

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2022187124

PROJECT CHARGE: 1706

PROJECT TITLE: TOBACCO PHYSICS

PROJECT LEADER: D. B. Losee

PERIOD COVERED: April 1-30, 1980

DATE OF REPORT: May 8, 1980

#### TOBACCO DECOMPOSITION STUDIES (1,2,3)

The development of computer software for manipulating DTG data is continuing.

The EGA-GC method is being adapted for a study of the effects of combustion on the evolved gases. Preliminary data on burley tobacco reveal substantial changes in the low temperature ( $< \sim 300^{\circ}\text{C}$ ) evolved gas profile compared to the pyrolytic situation. These same differences have been observed in the TG experiment.

#### CIGARETTE COMBUSTION/PYROLYSIS CONTROL (3,4,5,6)

Work continues on the effects that various salts have on the thermal decomposition of cellulose in pyrolysis and combustion.

The study of evolved TPM as a function of temperature has been extended to include combustion. Reproducibility during combustion is presently a problem. It is anticipated that the problem can be solved with proper flow control devices.

#### PHYSICAL CHARACTERIZATION OF TOBACCO (7)

Using reasonable assumptions about the physical properties of a shred of tobacco while in the expansion tower and the stated specifications for a Barnes Infrared Microscope a recommendation has been made to discuss the feasibility of using this device directly with Barnes Engineering Company.

#### MATHEMATICAL MODEL OF A BURNING CIGARETTE (8,9,2)

The particle size model, derived from considerations of the growth of droplets in a saturated solution, was subjected to a sensitivity analysis to identify the most important factors in the model. The most sensitive variables in the model were gas phase concentration, condensation temperature and age of the aerosol. The model will be tested against data from a dibutyl phthalate aerosol.

A new method for the determination of the particle size distribution in aerosols has been found. The method does not require an assumption to be made a priori about the functional form of the distribution. It appears possible that collection of the required data can be obtained with some modification to the present light scattering technique.

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The calculation of the transport properties of cigarette gas mixtures has been undertaken. These will be used to predict the flow field inside a cigarette.

APPLIED SPECTROSCOPY (9,10)

The currently available computer software for the Near IR blend analysis has been carefully examined and found adequate for our purposes. The necessary reflectance data for the various pure blend components are currently being acquired.

REFERENCES

- 1) J. F. Bebb, Notebook 7449.
- 2) K. R. Squire, Notebook 7440.
- 3) B. E. Waymack, Notebook 7482.
- 4) B. E. Waymack, "EGA of Cellulose Oxidized with  $\text{KMnO}_4$ ," memo to C. O. Tiller, April 30, 1980.
- 5) C. O. Tiller, Notebook, 7441.
- 6) P. E. Phillips, Notebook 7469.
- 7) C. O. Tiller and J. Lephardt, "Tobacco Shred Temperature in the Expansion Tower," memo to Mr. Fran Utsch, May 6, 1980.
- 8) D. L. Simpson, Notebook 7141.
- 9) K. A. Cox, Notebook 7507.
- 10) P. A. Wilson, Notebook 7365.

/ev

*D. E. Sall*

2022187126

CHARGE NUMBER: 1708  
PROJECT TITLE: Physical and Chemical Properties of Tobacco  
PERIOD COVERED: April 1-30, 1980  
WRITTEN BY: B.C. LaRoy  
DATE OF REPORT: May 8, 1980

#### MOLD GROWTH ON ET (J.C. Crump)

In last months report, the results of an investigation on the possible occurrence of mold on ET were presented for samples maintained at various moisture levels at 24°C. This study has been continued at 30°C with samples having equilibrated OV's of 12.8%, 14.5%, 18.8% and 20.0%. After six weeks, no mold has been observed macroscopically on any of the samples.

#### BRIGHT AND BURLEY LEAF CURLING (J.C. Crump)

Exploratory experiments have been initiated to determine the degree to which bright and burley leaf curl as a function of moisture and heating temperature. These studies are undertaken to provide assistance to Mr. Karl Jockel of Louisville Stemmary in determining if curling of the leaves processed through the Proctor & Swartz dryer can be minimized.

#### MECHANICAL PROPERTIES OF FILLER - Instron Testing to Simulate Maker (D.A. Full)

Experiments using the instron for uniaxial compression of bulk filler in a manner that mimics the specific volume vs. time for tobacco in a cigarette maker have been continued. From the latest runs, at a higher moisture than any previous runs, the only affect of higher moisture seems to be a reduction in pressure, by a factor that is nearly independent of the timescale and degree of over-compression. The pressure-reduction penalty attributed to momentary overcompression persists at the higher moisture. From reviewing the several runs to date, the effect of  $n\%$  overcompression (i.e. momentary compression to a specific volume  $n\%$  smaller than the final specific volume) is a reduction in the pressure observed subsequently by as much as  $3n$  to  $5n\%$  below what is observed in a matching run without overcompression.

The several parameters involved in these experiments are now being examined as variables for a more complete study of these phenomena.

#### BRUISING OF BRIGHT LEAF (B.C. LaRoy and D.M. Puzio)

Experimental work is nearly completed on grade E55 leaf. At equivalent densities and moistures, this grade exhibited significantly less bruising than either E9 or E33. For example, at a density of 0.6 G/CC (corresponding to a 2,000 lb. bale) and an OV of 18%, the surface area bruised for E55 was about 25% that of E9 and about

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CHARGE NUMBER: 1708  
May 8, 1980  
Page Two

35% that of E33. Though the leaf has been kept in cold storage (~40°F) the reduced bruising may be due to aging effects. We plan to re-examine grade 9 leaf (also cold-stored) to check this.

#### BREAKAGE OF RCB (B.C. LaRoy)

At the request of the Tobacco Quality Standards group, we have made a qualitative check for breakage of thrashed RCB when dropped through considerable distances. Several hundred identifiable rectangular coupons cut from RCB were mixed with 2KG of the thrashed sheet. The mixture was then dropped repeatedly through 30 feet of 12 inch diameter pipe. Flow conditions varied from well separated "free fall" to dense plugs. The coupons were then removed and examined. No breakage was observed, though some fraying of edges occurred on a few coupons. While this test does not simulate actual manufacturing conditions, the results do suggest that long drops during processing will not lead to extensive attrition. While laborious, the coupon technique used here might be extended to manufacturing runs in order to evaluate actual breakage.

#### MATH MODELING (H.A. Hartung)

An IBM 5120 minicomputer has been delivered and successfully interfaced to the R&D Sigma computer. Programs from the "Account 79" modeling system have been transferred to the 5120. Some of these will need slight modifications to run on the IBM system.

After initial setup and testing, the 5120 will be installed at Westab so that process variables can be input on a regular basis. Data will then be transferred to the R & D computer for use in modeling the Westab process.

*B.C. LaRoy*

2022187128

CHARGE NUMBER: 1801  
PROGRAM TITLE: Tobacco Processing  
PERIOD COVERED: April 1-30, 1980  
PROJECT LEADER: F. V. Utsch

I. REORDERING OF MC DET (F. Utsch)

A vibrating conveyor has been installed in D Pilot Plant to develop spraying techniques that can be used in the MC to apply a portion of the reordering moisture at the tower exit. Lifting flights are also being installed in the ball impregnator to improve showering of the particles for further batch reordering rate studies on fresh MC DET. The MC split flow reordering trials at a 12 minute cylinder retention time are scheduled for the week of May 19.

II. EXPANSION TOWER DESIGN STUDIES

A. Gas/Particle Contact (High Speed Photography) (B. Donenfeld)

High speed filming of tobacco particle flow in the 3"x10" plastic rectangular ribbon tower is proceeding. Preliminary designs for a Venturi throat section and for deflectors at the exit portion of the elbow were completed.

B. Expansion Studies - 4" Tower (M. Mobrem)

Several additional air leaks and an electrical control problem have been corrected. DIET expansion trials at inlet gas temperatures up to 850°F are in progress using the short horizontal 4" tower. The first series of test results indicate that the product equilibrated CV/OV curve is fundamentally unchanged from that of the standard two elbow tangential tower. Sieve results indicate that very low breakage is occurring with the horizontal tower installation. Tests studying the effects of tobacco feed OV and impregnation pressure are being run.

A regression analysis was performed on reordered Westab ET CV/OV results. There were indications that product with higher levels of ammonia tend to give lower equilibrated CV levels at the same equilibrated OV. Further studies will address this observation.

III. DIET PATENT APPEAL (R. Z. de la Burde, P. E. Aument)

Demonstration tests were conducted April 15-18 with lawyers representing both PM and Airco in attendance. It was clearly shown on both the Phase II and the Phase III systems that degassing of the impregnated filler does not improve the tobacco filling power and that application of positive heating is required to attain permanent expansion. This point was verified both in CV and cigarette compacimetric testing. This evidence will be used in the appeal trial scheduled to begin on June 25.

IV. CARBAMATE POWDER ET (F. Utsch)

The bulker, feeder and conveyors for the 8" tower carbamate ET prototype system have been installed. Wiring of the electrical controls is in progress.

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V. NEW TOBACCO TREATMENTS

A. Freeze-Drying of Tobacco (B. Donenfeld)

Turgorizing levels of up to 250% by weight (DWB) have been achieved by using a large excess of water. Recycling of the excess water to reach a steady-state where no further leaching of solubles occurs is being studied. Bill Carter is examining the frozen turgorized samples to establish the degree of swelling achieved. Freeze-drying using only ambient heat is giving a 1.9% Karl Fischer OV after 18 hours treatment in the Virtis freeze-dryer. Dr. T. Laszlo is assisting in these studies.

B. Crimping of RL for Improved Filling Power (R. Z. de la Burde)

Crimping of base web and sized RL at two different moistures was accomplished with a single filament resistance heating unit; pressure was required to make pronounced crimps. Since the work was done manually, the crimps were approximately 1/4" apart. Crimped samples that were equilibrated and shredded on a laboratory shredder did not show an increase in CV over the control. These dissatisfying results were attributed to the spacing of the crimps being too large compared to the thickness of the shredded RL fibers, the pressure from the two cutting edges of the shredder being too severe, and the crimped edges of the RL being excessively brittle. Trials using intermeshing screen wire to accomplish crimping are planned.

C. Dielectric Drying of RL for Improved CV (R. Z. de la Burde, R. O. Ellis)

A memo outlining the heat requirements, capital equipment costs, the advantages and the disadvantages of the proposed process has been released. An economic analysis of the various potential processing modes is scheduled in order to determine how much CV gain would justify the application. An experimental program has been designed to test base web and sized RL as well as tobacco filler at various moistures in the fields of 2415, 315 and 27 MHz (Thermex/Solidyne Corporation).

D. Improved Tobacco Bale Handling (R. Z. de la Burde)

A preliminary economic analysis on the dielectric treatment for improved bale opening has been completed by TPI. Capital improvements of approximately \$670,000 and an annual operating cost of approximately \$216,000 - \$337,000 was projected.

VI. PATENT SUPPORT ACTIVITIES (R. Z. de la Burde; et al.)

The unresolved technical issues as well as the inventorship on the low pressure - high moisture CO<sub>2</sub> applications have been resolved. Technical assistance was given in preparation for the pre-trial conference on the DIET appeal. A reply to the foreign objections on PM 783 (mist reordering) was prepared.



F. V. Utsch

/jb

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CHARGE NUMBER: 1803  
PROGRAM TITLE: New Primary Processes  
PERIOD COVERED: April 1-30, 1980  
PROJECT LEADER: R. G. Uhl

## I. CONVEYING STUDIES

Tobacco attrition studies on the belt conveyor system were continued. ET breakage was examined at a dropoff height of 4 feet, with variation of bed depth, belt speed and number of recycle passes. It was determined that 9 passes are required in order to obtain results that are consistently repeatable. Five tests run at a belt speed of 1 ft/second and a 1" bed depth showed an average loss in % longs of 4.1 units. Testing at higher belt speeds (2.5, 4.0 ft/second) indicated a "dead spot" resulting from the steep angle ( $20^{\circ}$ ) associated with the 4 foot dropoff height. This caused the tobacco to tumble in place at the feed end of each conveyor rather than continue up the belt, limiting testing to extremely light loadings. Comparison of all results to date shows that dropoff height is the major factor affecting conveyor breakage. Testing of the belt conveyor system has been temporarily suspended due to transfer of the feeder system to the carbamate expansion process.

## II. ALKALOID REDUCTION

Ammonia/steam treatment of cut rag in the vertical steam tube (VST)/Adt dryer system showed alkaloid reductions of 30, 15 and 10% at tobacco rates of 60, 200 and 400 lbs/hour, respectively. The test grid was rerun at two VST residence times as well as at standard and reduced  $\text{NH}_3$  concentrations in the steam. This is intended to show repeatability and to minimize  $\text{NH}_3$ , both the added amount and the residual amount remaining in the tobacco exiting the dryer. Preliminary results show residual  $\text{NH}_3$  increasing with tobacco throughput. The previous test has shown alkaloid reduction inversely related to residual  $\text{NH}_3$  at the same progression of feed rates. Engineering design is in progress to equip the dryer with rotary locks. This will be required to increase steam/tobacco contact at the 1200 lbs/hour throughput necessary to simulate production tobacco loadings.

A modified MAG drum, with a column simulating the VST, has been put into service for small scale testing. This unit will facilitate a controlled study of the effects of residence time, steam rate and ammonia concentration in the steam on alkaloid reduction, and the effects of the first two parameters in removing residual ammonia.

  
R. G. Uhl

/jb

2022187131

CHARGE NUMBER: 1804  
PROGRAM TITLE: CO<sub>2</sub> Expansion  
PERIOD COVERED: April 1 - 30, 1980  
PROJECT LEADER: R. G. Uhl

## I. TOWER STUDIES

The second round of tower gas velocity experiments was completed (four gas velocities, each at three temperatures). This was to determine the effect of gas velocity on CV/OV relationships, chemical losses and breakage as well as to assist in the design of improved tower configurations. Analytical results are pending.

Sixteen batches were expanded for the aged tobacco study (age = 2 months). Analysis of this data and comparison with the zero time and one-month samples show that the increase in CV due to expansion has been changing with tobacco age when comparing equilibrated tower exit CVs to feedstock values. The  $\Delta$  CV of the thin grade tobacco is decreasing by 3 CV units/month while the bodied tobacco  $\Delta$  CV is increasing 1 CV unit/month. Equilibrated cylinder exit CVs are holding steady at 84 cc/10g for the thin grade and 68 cc/10g for the bodied, resulting in  $\Delta$  CVs of 51 and 39 units respectively on a reordered basis.

The Marlboro blend cigarettes containing pilot plant expanded Trinity ripper shorts (15% in DBC bright) were remade to resolve subjective discrepancies not detectable in the cigarettes made from 100% expanded material.

Sieve analysis of spot samples from the pilot and MC DIET plants shows identical % longs being fed to both towers. However, most pilot plant breakage appears to be taking place after the clump breaker (in the Vibrabin and conveyor system) while almost all MC breakage appears attributable to the clump breaker. These effects also hold for analysis on a longs + mediums basis. More extensive sampling is planned at both locations to verify this spot analysis.

Westab impregnated ET was expanded in the 8" tower to determine the effects of increased gas temperature in a tangential system. Runs were made at 550, 565, 600 and 615°F in that order. There was a short delay between the 600° and 615°F runs. Temperature was re-established gradually; nevertheless, the tobacco ignited at 615°F. Tower exit OVs were higher than expected, ranging from 4-5% at the lower temperature to 3.8% OV at 600°F and 2.7% OV at 615°F. Pilot impregnated material normally runs 3.8 - 4.0% OV at 540°F. Reordered equilibrated CV was 11 units better for the 600°F sample (CV/OV = 82.5/11.4). (No. 615°F CV sample was taken due to sparks.)

## II. REORDERING STUDIES

Pilot DIET was reordered by mixing the tower exit material (~2% OV) with a like weight of unexpanded feed material (20% OV). This eliminates water spraying for reordering and eliminates roaster drying for part of the unexpanded bright blend. Analytical results are pending.

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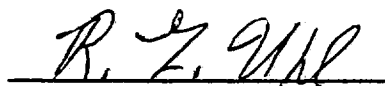
### III. ALKALOID RECOVERY

Alkaloid level in the wet scrubber liquor leveled out at just above 0.1%. Fresh water input and gas stream leaks have been eliminated to determine the maximum alkaloid concentration attainable in a total recycle system. Recovery of nicotine from the scrubber water via ion exchange resin appears to be the only viable recovery route with these extremely dilute solutions. Ammonia level in the liquor is 50 times greater with the ET process. This would necessitate  $\text{NH}_3$  removal for ion exchange recovery since it competes with nicotine for resin sites. Higher scrubber water alkaloid concentrations could make other recovery techniques (e.g. organic phase separation) feasible.

### IV. MISCELLANEOUS

The K-Ray unit has been relocated to the top of the impregnator. Circuitry repairs are in progress.

Demonstration runs were conducted for PM and Airco attorneys in reference to the DIET patent litigation.



R. G. Uhl

/jb

2022187133

CHARGE NUMBER: 1901  
PROJECT TITLE: Biochemical Modification of Tobacco  
PERIOD COVERED: April 1-30, 1980  
WRITTEN BY: D.M. Teng and B.A. Semp  
DATE OF REPORT: May 7, 1980

## I. Tobacco Aging Study

### A. Large Scale Aging Study<sup>1,2</sup>

The expansion by the Phase III DIET process of the third sets of samples from the aging study was completed. The results are being analyzed. Samples were also submitted for analyses. Microbial profiles of the samples were determined.

A special report, "Tobacco Aging Study I - The Baselines for 1979 Crop", was issued.

### B. Small Scale Aging Study<sup>2</sup>

The microbial profiles of the fifteenth month samples were completed. Other analyses are still in progress.

### C. Protein and Protease Study<sup>2</sup>

Isolation and determination of protease from the large scale aging study are being continued.

## II. Cellulase

### A. Waste Filter Tow and Cigarette Paper Treatment<sup>1</sup>

The concentration of KOH used for pretreating waste filter tow was studied. Waste filter tow and cigarette paper were treated with 0.25N, 0.5N and 1 N KOH, respectively. The samples were adjusted to pH 4.8 with glacial acetic acid, and treated with cellulase and cellobiase mixture. The degree of digestion and sugar formation were determined. It was determined that 0.5N KOH was adequate for pretreating waste filter tow materials for cellulase treatment.

A U.S. Patent application on treating cellulosic waste materials from cigarette manufacture was filed.

### B. Microstructure Determination of Cellulase Treated Samples<sup>3</sup>

Bright cut filler and strips (2.5 x 7.5 cm.) were treated

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with water, buffer or T.V. cellulase. Samples were dried and submitted to the Microstructure Facility for analysis.

C. Sugar Determination in Cellulase-Treated Tobacco<sup>3</sup>

In order to determine the type and amount of sugars or reducing groups formed in cellulase treated cut filler, bright cut fillers (as is and hot water extracted) were incubated in T.V. cellulase, citrate buffer or water. One set of samples were dried as is, another set separated into solid and liquid components. They will be submitted for glucose and total reducing sugar determination.

D. Cellulase Preparation<sup>4</sup>

A batch of T.V. cellulase was prepared. A portion of the enzyme was freeze dried.

III. Denitration - Pilot Plan

A. Smoke analysis data from 100% RL cigarettes which was denitrated by the anaerobic denitration pilot plant were completed. These analyses indicate that with regard to the measured parameters the materials denitrated with  $H_3PO_4$  were at least equivalent or better than those denitrated by other means.<sup>5</sup>

B. Preliminary data generated by "Chemap, Inc." and our own laboratory show that the "effigas" system for agitation is equivalent to the "New Brunswick" system. The "effigas" system is much less energy intensive and if the data continue to support its usage we will attempt to obtain permission for a much larger scale - up (65,000L) to further assess proposed engineering design criteria.<sup>6</sup>

IV. Denitration - Bench Scale

A. Process organisms were supplied to support the "Chemap" agitation studies.<sup>7</sup>

B. A study was attempted to denitrate tobacco extract containing 18% RI solubles and 3,000 ppm  $NO_3^-$ -N. The materials were "fed" at 10 and 14 hours to the inocula. Denitration was incomplete in both instances (<50%). We postulate

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an inhibitory effect on the insoluble materials in the extract. During the month of May we will attempt denitration of the extract after an additional liquor clean-up step.<sup>8</sup>

- C. A preliminary evaluation of  $H_3PO_4$  reduction in the tobacco substrate has shown that a substantial reduction in the use of acid can be obtained, (from 5.6 mls. to at least 3.0 mls./L). Further work will be done to reduce this acid level to no more than 1 ml. 85%  $H_3PO_4$ /L of tobacco extract.<sup>9</sup>

REFERENCES:

- |                                     |                    |      |
|-------------------------------------|--------------------|------|
| 1. D. Teng                          | P.M. Notebook      | 7418 |
| 2. G. Nixon                         | Notebook           | 7208 |
| 3. E. Mooz                          | Notebook           | 7443 |
| 4. S. Tenhet                        | Notebook           | 7225 |
| 5. Minutes of Meeting - Denitration | 4/18/80 Attachment |      |
| 6. H. Bravo                         | Notebook           | 7457 |
| 7. D. Chadick                       | Notebook           | 7628 |
| 8. H. Bravo                         | Notebook           | 7457 |
| 9. D. Chadick                       | Notebook           | 7628 |

*Dm Teng*  
*B. A. Semp*

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CHARGE NUMBER 2100  
PROJECT TITLE New Product Development  
WRITTEN BY Paul N. Gauvin  
PERIOD COVERED April, 1980

## I. NEW PRODUCTS

### A. Merit Ultra Lights

The best 3 mg, 85 mm candidate, the M+199, is currently in National POL testing versus Triumph. Preliminary results (37% returns) indicate the M+199 is preferred by 0-5, 5-10 and Merit Smokers. In the 10-15 mg category no preference is indicated. The M+199 has previously tested well against Kent III and other 3 mg candidates. Plans call for testing the 3 mg, M+199 versus Merit 85 and Kent Golden Lights.

Cigarettes are currently being made for two multipack tests where the M+199 will be compared to three 5 mg candidates and the Merit 85 in one test and Kent III in the other. The 5 mg candidates consist of a B&H Lights-type, a Merit-type and the M+199. The B&H Lights-type is currently in POL testing versus Vantage Ultra Lights. Preliminary results (31% returns) indicate the B&H Lights-type is preferred by 5-10 mg and Merit smokers. The Merit-type will also be POL tested versus Vantage Ultra Lights as soon as possible.

In the 100 mm configuration the M+199 is in POL testing at the 5 mg tar level versus the Kent III 100.

The POL multipack study containing a 100 mm M+199 and Trinity W, both at 4 mg tar, plus the Kent III 100 and Carlton 100 shows the 100 mm, M+199 candidate as being preferred with 0-10 mg smokers. The 10-15 mg smokers rated the Carlton 100 as being less preferred than the other cigarettes. Among Carlton smokers the M+199 candidate is preferred over the Kent III 100, Carlton 100 and Trinity W 100.

A 100 mm multipack study with experimental M+199, Trinity W, M+83E and M+11B cigarettes, all at 5 mg tar, versus the Kent 100 is also in the field. Results are expected in mid-May.

### B. Reduced CO Marlboro

The objective in this program is to maintain equal tar delivery to the regular Marlboro while reducing the CO delivery 25-30%. A special low efficiency, high RTD tow item from Celanese has been tested on a Marlboro cigarette with increased dilution to achieve the objective. A cigarette with this special tow has been developed and has tested favorable on VP and POL against a Marlboro control. We plan to rerun a POL test of the reduced CO Marlboro candidate versus Marlboro 85 due to cooling notes observed in the first POL.

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Models have also been made to compare cigarettes with the low efficiency, high RTD tow versus more conventional tow items. The special Celanese filter appears to give a higher tar delivery but lower RTD than the other models.

#### C. Project Mild

Our objective in this program is to develop an alternate to Merit in the 7-9 mg tar range that has flavor with mildness. Initial models have been made for in-house evaluation and include blends with various levels of burley leaf and the Marlboro blend with modified flavors. Internal screening will be conducted and additional models made. Consumer testing versus Merit and Kent Golden Lights will be conducted by the 3rd or 4th quarter, 1980..

#### D. Polypropylene Filter Material

Several bales of polypropylene tow have been received from Hercules and evaluated on the Eastman miniature plugmaker. Compared to CA filters of the same pressure drop, we are not equal in filter efficiency. Maintaining an acceptable filter firmness at a reasonable RTD is also a problem. However, a cost advantage with polypropylene versus CA fiber does exist and warrants continuing the evaluation of the polypropylene as a filter material. Discussions are being held with Hercules personnel to arrive at acceptable solutions to the filter efficiency and firmness problems with this new tow.

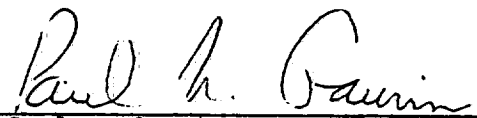
### II. SMOKER SIMULATOR

#### A. Basic Studies

A Simulator study has been initiated on the investigation of the effect of high dilution (50+%) upon smoker parameters and deliveries.

#### B. Product Studies

A smoker response study is in progress on selected 5 mg B&H Lights-type and Merit-type candidates versus Merit and Vantage Ultra Lights. In addition, a study of a 3 mg M+199 candidate versus Kent III, Triumph, and Merit 85 has been partially completed through the preparation of Simulator Command tapes.

  
Paul N. Gauvin

/ksj

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CHARGE NUMBER 2100  
PROJECT TITLE New Product Development  
PROJECT LEADER Paul Gauvin  
PERIOD COVERED April, 1980  
WRITTEN BY W. E. Claflin

I. PROJECT TRINITY (CAMBRIDGE)

This is the last monthly report in which Cambridge program will be covered separately. In the future the program will be included in the regular New Product Development report.

The initial production orders have been met for all three Cambridge products with satisfactory product being made in all cases. Reorders have been or are now being made for the products. Consumer sales results are not now available.

The King Size box product has been redesigned with higher dilution to minimize the tar delivery from this product.

Menthol companions for the King Size soft pack and 100 mm soft pack products are in the design and flavor development stage. A test market for these products is expected later in the year.

/ksj

W. E. Claflin  
(PG)

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CHARGE NUMBER 2105  
PROJECT TITLE Filter Development  
PROJECT LEADER W. A. Nichols  
PERIOD COVERED April, 1980

## I. WRAPLESS FILTERS

### A. Microwave Process

Filter samples (2.5/48,000) were produced via the microwave process for filtration efficiency studies. Initial analysis of tow yield indicates less yield loss (RTD/Tow wgt.) on 2.5/48,000 processed with microwave than with the Filtrona process.

Attempts were made to bond polypropylene fibers with microwave energy. Heat transfer to the fiber from the liquid phase absorbing medium was insufficient to melt the fiber at points of contiguity. Other liquids will be tested as possible bonding agents.

### B. Filtrona NWA Process

Filter samples were produced for adhesive testing and a tip firmness vs. filter firmness study. Analysis is in progress.

Plasticizer droplet size has been defined as a process variable. To permit investigation with various droplet sizes the Filtrona plasticizer system was removed and a Hauni system is being installed. Larger droplets tend to make a firmer filter.

Several tests were conducted at the Manufacturing Center. Adhesive samples, Ajax 634 and Swift K9288, were evaluated at 4500 Cigts/min. Poor adhesion was observed with both samples. Adhesive age and contamination may have been a factor in the test. New samples are going to be evaluated. Tests were run on WJ4 NWA plugmaker to evaluate the Filtrona stuffer jet that transports the tow from the tow prep unit to the garniture. Results indicate improved product quality. Recommendations were made to Manufacturing Engineering to replace Eastman jets with Filtrona jets on NWA plugmakers.

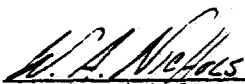
## II. MENTHOL APPLICATION

Aging studies of the first sample run were completed. After four weeks less than .01 mg of the 65 mg of menthol remained on the pack foil. Menthol analysis shows 3.1 - 3.5 mg in the filler and filter and .18 mg of menthol delivered in smoke. A second set of samples were produced and are being shelf aged and analyzed.

## III. EXTRUDED TOBACCO

To determine if continuous rather than batch mixing is possible, several suppliers of continuous Banbury type mixers were contacted. Arrangements are being made to evaluate a continuous mixer.

/ksi

  
W. A. Nichols

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PROJECT CHARGE: 2106  
PROJECT TITLE: APPLIED TECHNOLOGY  
PROJECT LEADER: Peter Martin  
PERIOD COVERED: April 1 - 30, 1980  
DATE OF REPORT: May 8, 1980

#### PERFORATION OF TIPPING PAPER

The production of perforated tipping paper for the national introduction of the Trinity brand has been completed. During the introduction the parameters for the 83 mm box product were changed. Bobbins were made to determine the new parameters and then the production requirements met under very short notice. Tests were run in conjunction with Judy Nash of Operation Services to determine a realistic pressure drop range which would maintain the target dilution range. Bobbins of Virginia Slims and Saratoga tipping paper were perforated to determine likely running parameters if it should be decided to laser perforate these products in-house. Support has also been given in perforating paper for new product development.

Three laser systems are now successfully running at DMPC and are being used to perforate paper for the Trinity brand and the Protos made Merit brand. Assistance was given in aligning and tuning up the lasers, and in setting up the running parameters. Union employees are now being used to operate the systems and short talks on laser safety were given to each of the shifts. Future plans call for hourly personnel to assist in maintaining the lasers and detailed plans have been made for their training.

Working with Neal Nunnally, Optical Porosity Monitors (OPM) have been installed on the DMPC systems. These are prototype systems and still have problems with respect to linearity, uniformity of beam and dust accumulation, but it is felt that they are capable of detecting short strips of paper where the perforation is bad. Improvements under investigation are the use of larger lenses and the use of a cylindrical lens in conjunction with a line light source.

Experiments were run to determine whether it was possible to eliminate the expensive adjustable stand for the lasers and to do the beam steering by output coupler adjustment. It was found that the adjustment via the output coupler is very coarse and in practice cannot move the beam more than 2 inches at the location of the optical system.

#### METAL DETECTORS

A visit was made to Steinbrecher Corporation in Boston to see his production capabilities and to see a demonstration of his antenna design and tuning. His proposal was discussed in detail and working with Engineering a detailed

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set of requirements for a case inspector is now being prepared.

HEAT TREATMENT OF RL

Some experiments have been started to investigate the effects of high temperature oven heating on RL. Previous experiments were conducted at 180°C and results are now being obtained at 250°C. A temperature of 310°C seems to be too hot and produces degradation of the RL sheet.

A sample of RL has had the Toluene-Ethanol soluble fractions removed and will be used for low temperature oven heat treatment. This is part of a program to determine the components in tobacco which are responsible for the cross-linking.

Purchase orders have been placed for lamps and controller to set up bench scale expansion experiments.

*Peter Martin*  
ev

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2022187142

CHARGE NUMBER: 2305  
PROGRAM TITLE: Flavor Development  
PROJECT LEADER: J. W. Swain  
PERIOD COVERED: April 1-30, 1980  
DATE OF REPORT: May 6, 1980  
WRITTEN BY: J. W. Swain and L. Wu

I. R. L. Flavor

Cigarettes for HTI tests of the Y79-3 Marlboro, Y81-1 Marlboro with Y79-3 level of ET, and Y81-1 Marlboro with RL and ES at Y79-3 levels will be remade due to differences in deliveries. Results of V-3813 evaluating the Y78-4 versus the Y81-1 Marlboro have shown no significant differences. Test Y81-1 Marlboro blends with 15% ET versus 15% DET showed no differences except the female subgroup preferred cigarettes with 15% ET. Mainstream  $\text{NH}_3$  values tend to be higher from Y81-1 than from Y78-4 Marlboro blends. Preliminary results of V-4755 testing the Y78-4 Merit against Y81-1 Merit show subgroup differences in aftertaste and preference.

Additional Pilot Plant trials were made with prorated 150 $\beta$  flavor levels and  $\text{NH}_3$  precursor reductions. These are currently being evaluated in Y81-1 Marlboro blends.

II. Reaction Flavors

National Panel tests 3120 and 3122 with Y78-4 Marlboro control versus Y81-1 Marlboro containing Reaction Flavored RL's 563 and 564, respectively, will be mailed this week.

After eleven weeks of storage at room and refrigerated temperatures, no significant changes have been observed in the levels of original reactants.

III. Services to Other Groups, Manufacturing and PMI

Reaction Flavors were screened on Flue cured Brazilian stems. They were sprayed on stems in the lab and evaluated in 100% stem cigarettes. Two of the flavors (7397-97 and 7396-147) showed improvements by reducing the harshness and stem character. The flavors were sent to Brazil for further

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evaluation on stems in the Brazilian blends.

A report was made to evaluate a 3% Det overfeed in Manufacturing Center Marlboro filler compared to regular Manufacturing Center and Stockton Street Marlboro fillers. No significant differences were found by the Flavor Group and SEF panels at the 95% level ( $p > .05$ ) for the following:

Manufacturing filler vs. Stockton Street filler

Manufacturing filler vs. 3% Det overfeed

Stockton Street filler vs. 3% Det overfeed

#### IV. References

##### Notebook Pages

7396-136-156

7397-107-120

*J. W. Swain*

J. W. Swain

*L. Wu*

L. Wu

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CHARGE NUMBER: 2306  
PROJECT TITLE: Flavor Transfer  
PROJECT LEADER: R. M. Ikeda  
PERIOD COVERED: April 1-30, 1980  
DATE OF REPORT: May 7, 1980  
WRITTEN BY: R. M. Ikeda

### I. Oriental Flavor

An investigation was carried out to compare Fraction 5 which contains the characteristic Oriental smoke flavor from samples of MF Oriental blend and Thai Oriental tobacco. The acids liberated from Fraction 5 with sodium hydroxide showed a peak height ratio of 2/1 of  $\beta$ -methylvaleric acid/valeric acid for the Thai Oriental tobacco and a ratio of 5/1 for the MF Oriental blend. This higher ratio of  $\beta$ -methylvaleric acid/valeric acid may be an indication of the higher Oriental smoke flavor and sidestream odor observed in the MF Oriental blend.

In order to obtain a larger sample of Fraction 5 for identification of the material responsible for the Oriental smoke flavor, two samples of the best grade of Oriental tobacco are being investigated.

### II. Burley Flavor

A 200 g sample of Burley tobacco was extracted with methylene chloride. The extract was separated into acid, base and neutral fractions. The neutral fraction was steam distilled and extracted with methylene chloride. The distillate was separated by silicic acid column chromatography into 12 fractions. Fractions with best odors were 7, 8 and 9. Fraction 8 was separated packed column GC and the "peaks" were collected. These collected fractions were rechromatographed on glass capillary GC/MS. Over 100 "peaks" were identified by GC/MS in fraction 8.

### III. References

1. Notebook #7464, pp. 25-30
2. Notebook #7483, pp. 5-14

  
R. M. Ikeda

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CHARGE NUMBER: 2500  
PROGRAM TITLE: Synthesis of Tobacco Additives  
PERIOD COVERED: April 1 - 30, 1980  
PROJECT LEADER: J. I. Seeman  
DATE OF REPORT: May 8, 1980

## I. FLAVOR CHEMISTRY

A major effort is underway to prepare 10 pounds of a key oriental flavorant. This substance has shown interesting subjective results at relatively low threshold levels. A number of different chemical steps are required to prepare the material from commercially available and inexpensive reagents. Because of the very large scales involved, the procedures are rather laborious and significant care is being taken to insure positive results.<sup>1-3</sup>

The novel process used to prepare 2-isopropyl-5-keto-hexanoic acid from piperatone was used to prepare a number of additional keto acids from readily available cyclic  $\alpha,\beta$ -unsaturated ketones. A literature search was carried out and there is no prior art regarding this oxidation procedure.<sup>2</sup>

Ethyl vinyl ketone and isopropyl vinyl ketone were each reacted with the pyrrolidine enamine of isovaleraldehyde to give the corresponding 2-isopropyl-5-ketoheptanal and 2-isopropyl-5-keto-7-methyloctanal. These materials will be oxidized to the related keto acids which are analogues of 2-isopropyl-5-ketohexanoic acid. The alkyl vinyl ketones were prepared by reaction of the alkylcarboxylic acids with vinyl lithium.<sup>4</sup>

Approximately 2.5g of 12Z-abienol was obtained from careful HPLC purification of a small portion (5g) of oil isolated from 200g of Canadian balsam. Some 50g of the oil remains for additional preparation the 12Z-abienol which was identified by  $^{13}\text{C}$  nmr spectroscopy. Abienol is expected to be

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a key precursor of a number of potentially interesting tobacco flavorants. Effort is also being made to use this labdane terpenoid as the starting point for the preparation of terpenoid flavorants found in a variety of tobaccos.<sup>5</sup>

Reaction of methylpyrazine with LDA/isopropylbromide gave isobutylpyrazine (15%) along with two new pyrazines, 2,3-diisobutylpyrazine and 2,4-dimethyl-3-pyrazylpentane, a highly branched, monosubstituted pyrazine. The latter has a tea-like aroma similar to Bright tobacco. All three will be evaluated shortly.<sup>5</sup>

Menthylmagnesium chloride was reacted with *t*-butylisocyanate to give a mixture of WS-14 and neo-WS-14. A large sample of ethyl 2-sec-butyl-3-hydroxy-3-phenylbutanoate, an ethyl  $\beta$ -methylvalerate:acetophenone release agent, was prepared.<sup>1</sup>

## II FLAVOR RELEASE

The two major products resultant from the self-condensation of 3-acetylpyridine have now been identified as the dimeric 3-pyridyl 2-(3-pyridyl)-1-propenyl ketone and the trimeric derivative, the latter presumably formed by the addition of the anion of 3-acetylpyridine to the dimer. Pyrolysis of the sodium salt of 2-sec-butyl-3-hydroxy-3-(4-pyridyl)butanoic acid gave 4-acetylpyridine and sodium  $\beta$ -methyl valerate. No olefin, which would have resulted from dehydration, was observed. Nonetheless, the pyrolysis was not as clean as that found for the 3-pyridyl analogue.

Sodium 2-(sec-butyl)-3-hydroxy-(3-pyridyl)butanoate was impregnated on cellulose filter paper and subjected to the standard pyrolysis conditions; significant quantities of  $\beta$ -methylvaleric acid and 3-acetylpyridine (1:1) was obtained along with a trace amount of the dehydration product. This demonstrates that the salt releases the free acid in the presence of water.<sup>6</sup>

In a most unusual result, the reaction of phenylacetone with diethylcarbonate and sodium hydride led to a mixture of phenylacetic acid and diethyl phenylmalonate. An interesting series of reactions has been proposed to account for the results. Further attempts to prepare a ketone release agent are in progress.<sup>7</sup>

The reaction of a number of carboxylic acids with simple sugars in the presence of carbonyldiimidazole affords sugar esters of unknown structure. Careful nmr analysis has not yet allowed the determination of the position(s) of esterification. These materials are expected to provide interesting acid release systems.<sup>7</sup>

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Approximately 400g of poly(monomenthyl itaconate) has been prepared. Hydrogenation of the product is being completed to remove any residual monomer unsaturation.<sup>8</sup>

1-O-(3-methylvaleryl)- $\alpha$ -D-mannopyranose was prepared in a number of steps from  $\beta$ -methylvaleryl chloride and the protected mannopyranose derivative. This will be tested as a  $\beta$ -methylvaleric acid release agent. It has the particular advantage of being water soluble and mostly "sugar-like."<sup>8</sup>

Preparation of vinyl ethyl *sec*-butylmalonate was carried out. This material was polymerized and will serve as an ester release agent, in this case releasing ethyl  $\beta$ -methylvalerate.<sup>5,8</sup>

### III ALKALOID CHEMISTRY

The reaction of 3-pyridyllithium with N-methylpyrrolidinone followed by acid treatment and extensive purification led to a beautifully crystalline sample of N'-methylmyosmine diperchlorate. Conditions were found to obtain 2'-methylnicotine from the above diperchlorate by reacting it with 0.95 equiv of methylolithium at low temperature.<sup>9</sup>

Two very interesting 6-substituted nicotine analogues have now been prepared: 6-isopropylnicotine and 6-cyclopropylnicotine. These are particularly valuable due to the structural similarity of an isopropyl group and a cyclopropyl group. As part of a study aimed at determining the racemization step in the asymmetric nicotine synthesis, (S)-(-)-1-methyl-2-cyanomethylpyrrolidine was treated with LDA under the previously used alkylation conditions; recovered starting material (75%) had an identical rotation to that observed before the reaction. Efforts continue toward the preparation of additional bridged nicotines. Alkylation of 7,8-dihydro-5(6-H) quinolone with LDA/*t*-butylbromoacetate led to alkylated product in 50% yield. Attempts to reductively aminate this keto ester failed.<sup>10</sup>

### IV. REFERENCES

1. DeBardleben, F. 7310
2. Edwards, W. B. III, 7415
3. Because of the nature of this project, a major group effort is being undertaken to lend assistance whenever required.
4. Williams, D. 7448
5. Southwick, R. 7446
6. Houminer, Y. 7424
7. Chan, G. 7341
8. Grubbs, H. 7361
9. Secor, H.V. 7386

Jeffrey Seema

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2022187148

CHARGE NUMBER: 2501  
PROGRAM TITLE: Nuclear and Radiochemistry of Smoke  
PROGRAM LEADER: Roger A. Comes  
PERIOD COVERED: April 1 - April 30, 1980  
DATE OF REPORT: May 5, 1980

I.  $^{14}\text{C}$ -Altosid<sup>1</sup>

The results reported in the previous monthly report in regard to Altosid migration during the past ninety days have been verified by resampling and recounting. Specific evidence as to the course of this sudden migration after approximately two years has not been forthcoming. However, it should be noted that the room in which the experiment was run has recently experienced fluctuations in temperature and humidity. This is in contrast to the constant conditions maintained during the bulk of the experimental time frame and must therefore be considered in the final overall evaluation of this study.

II. Low Level Laboratory and Greenhouse<sup>1,2</sup>

An engineering consultant has been contracted to aid in evaluations directed toward the construction of the low level laboratory and the greenhouse expansion project. Considerable progress has been made in both of these areas. Trips to the Tennessee Valley Authority Radiological Laboratory, to Oak Ridge, Tennessee and to Carolina Power and Light Energy and Environmental Center have been highly informative in the future construction of a low level laboratory. Discussions with personnel at these laboratories were involved with lab design, detectors and detector systems, low level counting statistics, plating techniques, etc. A proposal for construction and equipment to be employed in this laboratory is presently being prepared.

Efforts in the greenhouse expansion project have centered on specifications, utilities, equipment cost estimates, etc. This preliminary planning is also nearing completion with construction hopefully to begin during 1980.

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III. Glanded and Glandless Tobacco<sup>2,3,4</sup>

Samples of glanded and glandless tobacco grown at the Oxford, N.C. Experiment Station have been received, hand stemmed and machine made into 85mm non-filter cigarettes. Ecusta 351 paper was used with 2.8% glycerine and 5.3% invert sugar as the only filler additives. Samples have been submitted for filler and smoke analyses to investigate possible differences related to the presence or absence of the tobacco gum exudate which forms at the end of the trichomes on the glanded tobacco. Trichomes are present on the glandless tobacco but the gummy exudate does not form at the trichome ends. The cigarettes and WSC from the two samples will be evaluated for the presence of and difference in levels of natural radioactivity.

IV. CO Delivery<sup>5,2</sup>

a. The work concerned with the formation and delivery of CO as it relates to cigarette paper additives has continued. It has previously been shown that cigarette paper with MAP additive delivers some 50% more CO than either untreated or citrate treated paper.

In last month's report the statement was made that there appeared to be a relationship between coal temperature and CO delivery. A reexamination of the data does not support this supposition.

There was no difference in the coal temperature between the citrate additive paper and the phosphate additive paper. There was, however, as noted above a great discrepancy in CO delivery.

In an attempt to further elucidate the association between additives and CO delivery, a pyrolysis experiment was carried out. Samples of cigarette paper (2mg) were pyrolyzed at 800°C under He and CO and CO<sub>2</sub> separated by G.C. The results of this experiment were inconclusive and the experiment will be repeated in an air atmosphere to more closely approximate the normal conditions.

b. Central core cigarettes - In line with efforts to reduce CO in mainstream smoke, special cigarettes have been fabricated containing central rods or cores made of various materials. The cigarettes are Merit type, using Merit filler, paper, and filters. Analyses of control cigs (hand made Merit), and experimental cigs containing cores made of 3mm tobacco material, 4mm

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tobacco material, 4mm pith wood (elder), and 3.5mm solid carbon showed reductions in the ratio of CO/Tar of 22%, 37%, 40%, and 73% respectively. Possible patent applications for this idea are being investigated.

V. Miscellaneous<sup>2,3,4,6,7</sup>

a. Potassium rate study - A total of 24 stemmed leaf tobacco samples from the 1979 potassium rate study have been received. This test consisted of six rates of potassium (0, 30, 60, 90, 120, and 240 lbs per Acre) times four replications grown on the Whiteville, N.C. Experiment Station. This tobacco will be blended based on yield by priming and made into cigs for smoke tests to determine if burning rate and other smoke components are related to the potassium content. This is the third and final crop year for this series of agronomic tests.

b. Fresh green tobacco plant materials were supplied to: 2501, Analytical Services; Manufacturing Center; Administrative Services and Engineering Services.

c. Instrument repair, maintenance, and updating continues to occupy a major time effort. A test and maintenance area have been set up to try and keep the instrumentation (much of which is 10 years old or older) in operating condition.

d. The new Beckman 7500 Liquid Scintillation Counter has been received and is currently being checked out before it is put into routine operation.

VI. References:

1. A. Frisch - N.B. 7309
2. R. Bass - N.B. 7296
3. A. Durant - N.B. 7435
4. G. Newell - N.B. 7295
5. R. Newman - N.B. 6549
6. B. Francis - N.B. 7486
7. G. Segura - N.B. 7502

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2022187151

CHARGE NUMBER: 2525  
PROJECT TITLE: Chemistry & Isolation of Tobacco  
Constituents  
PERIOD COVERED: April 4 to May 5, 1980  
PROJECT LEADER: S. A. Haut  
DATE OF REPORT: May 6, 1980

The polymeric release model, poly- $^{14}\text{C}$ -isopropenyl 2-ethylhexanoate ( $^{14}\text{C}$ -poly PEX) (in conjunction with Harvey Grubbs, Project 2500) has proven to be a difficult radiochemical synthesis.<sup>1,4</sup> The polymerization step on the first batch of this material (42mg, 632 $\mu\text{Ci}$ ) resulted in a considerable loss of the radiolabel in the crude polymer (170 $\mu\text{Ci}$ ). Some residual activity could be found on the glassware used (<60nCi) but not of sufficient quantity to account for the loss. As a result, a second batch of  $^{14}\text{C}$ -PEX monomer was made and purified as before. The mass and activity yields were essentially identical (51mg, 940 $\mu\text{Ci}$ ). Polymerization of this material also resulted in considerable loss of activity (430 $\mu\text{Ci}$  in crude polymer). This time however, condensation was noted on the inner walls of the vessel. When checked for activity this material which was quite volatile contained much activity. At this time we do not know why or how this is occurring.

What polymer we have has been characterized by Mayada L  gue (Project 1703). Altogether, about 50% of the crude combined polymer is of molecular weight 800 and above. At this time, the polymer is being purified by GPC and will be applied to tobacco for smoke studies. GLRC preliminary work is already in progress.

During the past month, five samples were run on the preparative HPLC for Project 2500.

7446-46, 7393-109a  
7341-162, 7386-152-1  
7341-179

We are currently conducting a trial project exploring the isolation and identifications of components in a browning mixture by TLC and HPLC.<sup>5</sup> We have achieved the isolation of several materials but their composition or identity as yet

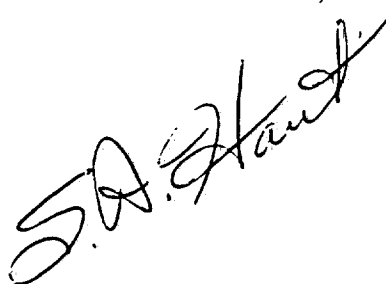
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is unknown. GC-MS assistance is being given by Project 0108 on this work and in identifying the by-products from the synthesis of PEX.

## References:

1. Barlow, K. R.
2. Core, M. T.
3. Chavis, M. K.
4. Haut, S. A.
5. Edmonds, M. D.

A handwritten signature in black ink, appearing to read "S.A. Haut", is written diagonally across the right side of the references list.

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CHARGE NUMBER 4009  
PROJECT TITLE Paper Development  
PROJECT LEADER W. A. Geiszler  
PERIOD COVERED April, 1980

### I. LASER PERFORATING

Assistance was provided to start up the laser perforating operation at the 19th Street plant. Three laser perforators have now been set up and are being used in production for Merit and Cambridge tippings. Three shift operation is scheduled to start in mid-May. A fourth perforator is to be set up at 19th Street in May.

Laser perforation for product development work has been resumed at the Midlothian building. Tippings have been produced for evaluation on Virginia Slims Lights, Marlboro LS, Saratoga, and several new product prototypes.

### II. ELECTRICAL PERFORATING

Cigarettes made with an electrically perforated experimental cork tipping colored with iron oxide, GSR-IC-1, have been found to have nearly invisible perforations and a good cigarette appearance. The tipping is being re-evaluated to see if it can meet our color standards.

### III. WRAPPER COMPOSITION

#### A. Low Sidestream Wrapper

An experimental wrapper from Ecusta for sidestream reduction containing 5% glass fibers has been evaluated for gas phase delivery. Results of smoking handmade cigarettes shows higher CO per puff deliveries for this wrapper than for regular cigarette wrappers but less than for previous low sidestream wrappers submitted by Ecusta. This wrapper contains MgO as a filler instead of  $\text{CaCO}_3$  and acetate burn additives instead of citrates. Additional samples will be requested.

#### B. WS-14 Wrappers

Experimental wrapper hand sheets have been made incorporating WS-14 cooling compound in the furnish. A wrapper containing WS-14 at the 7 mg per cigarette loading rate has been made for evaluation by the Flavor Division.

Wrappers coated with an alcohol solution of WS-14 have also been made at loadings of 8-9 mg per cigarette. The Greiner porosity of the coated wrappers is about 35 seconds versus 8-12 seconds for the uncoated wrappers. The Flavor Division will also evaluate the coated wrappers.

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#### IV. TIPPING FLARE-UP PROBLEM

A large number of cigarettes have been smoked on a smoking machine to try to determine the cause of the tipping bursting into flame as noted in several letters of complaint. The phenomenon has been observed on two cigarettes by puffing when the coal is under the tipping at the tobacco rod - filter junction. It appears that channeling of the smoke along one side of the filter also accompanies the flare-up.

*W. A. Geiszler*

W. A. Geiszler

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CHARGE NUMBER 4010  
PROJECT TITLE Brand Development  
PROJECT LEADER W. G. Houck  
PERIOD COVERED April, 1980

## I. BRAND DEVELOPMENT

### A. Marlboro/Marlboro Lights King Size Box

Since preliminary testing was successful, test markets are now planned for both the Marlboro and Marlboro Lights 83 mm Box products. Marlboro Lights Box test market will begin in July with Marlboro to follow in September or October, 1980.

### B. Filter Length Changes

Specifications were to be transferred to Manufacturing for the Virginia Slims (25.0 - 27.5 mm). Additional POL testing will be done on the Marlboro Lights and Merit.

### C. Lights 100's Tar Reduction

Nine (9) mg models of B&H Lights 100, Merit 100, Marlboro Lights 100 and Parliament 100 have been made and tested analytically. Subjectively, however, satisfactory models have only been produced for Merit and Marlboro Lights 100.

## II. COMPONENT EVALUATION/QUALIFICATION

### A. Celanese Triacetin

Additional consumer testing<sup>1</sup> was initiated and cigarettes have been made. Analytical data should be available by 5/15/80.

### B. Cigarette Paper

Results of an initial study of production cigarette paper interchangeability were presented to Manufacturing operations. Further tests using selected papers from the Manufacturing Center will be conducted.

<sup>1</sup>POL 3129

  
W. G. Houck

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CHARGE NUMBER: 6906  
 PROJECT TITLE: BIOLOGICAL EFFECTS OF SMOKE  
 PERIOD COVERED: April 1-30, 1980  
 PROJECT LEADER: R. A. Pages  
 DATE OF REPORT: May 5, 1980

1. SALMONELLA/MICROSOME ASSAY

A. Expanded Bright WSC Activities<sup>1,2</sup>

To confirm and extend results obtained last year,<sup>3</sup> a new set of cigarettes containing expanded bright tobacco was fabricated specifically to examine the effects of cylinder reordering with and without blow-box equilibration on ET (NH<sub>3</sub>/CO<sub>2</sub> expansion process) and carbamate ET (ammonium carbamate expansion process) WSC activity. The results (which included a statistical analysis conducted by J. E. Tindall) were as follows.

<u>WSC</u>	<u>TA98 Activity<sup>1,2</sup></u>
ET (blow-box equilibrated)	1300
ET	1252
Carbamate ET	1256
Carbamate ET (blow-box equilibrated)	1106
Westab Feedstock (Control)	954
DET (MC)	692

1) TA98 Activity (revs/mg of WSC): mean of determinations conducted on four separate preparations of each WSC in the presence of microsomes.

2) Samples not within the same bracket are different,  $p < 0.05$ .

The overall results were consistent with those previously reported; *i. e.*, tobacco expanded by the two processes which lead to increased levels of filler nitrogen (ET and carbamate ET) yielded WSCs of increased activity (relative to their unexpanded control WSC). In contrast, tobacco expanded by the liquid CO<sub>2</sub> process (DET), which does not affect the level of filler nitrogen, yielded a WSC of reduced activity.<sup>3</sup> The blow-box equilibration treatment had no effect on ET WSC activity. However, for carbamate

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ET, the blow-box equilibration treatment significantly reduced WSC activity. The reason(s) for the latter result is obscure, but it may be that the reduction in filler nitrogen which accompanied blow-box equilibration of the carbamate ET is associated with this phenomenon. (Blow-box equilibration of ET slightly increased filler nitrogen.)

B. Denitrated RL WSC Activities<sup>4</sup>

Tests were begun on a series of WSCs derived from nine different 100% RL cigarettes which represent each of the denitration processes currently being used or evaluated at PM. In the first experiment, which involved tests in strains TA98 and TA100  $\pm$  microsomes, no unusual features were observed in the activity profiles of any of the samples. A second experiment is in progress to establish the relative activities of the nine samples based on testing four replicate WSC preparations from each cigarette type in TA98 (+ microsomes).

2. YEAST MITOTIC GENE CONVERSION ASSAY<sup>5</sup>

A. WSC Fractions (with 6908)

To extend our knowledge about base fraction activity,<sup>6</sup> a set of burley WSC fractions was tested: the basic fraction and the methanol (MeOH) and ether eluates obtained from alumina column chromatography of the bases.<sup>7</sup> The results showed that: the MeOH eluate contained the bulk of the basic fraction activity; the ether eluate was only weakly active; and the MeOH eluate was less active than the basic fraction. Except for the latter result, these conclusions were similar to those obtained in the *Salmonella*/microsome assay.<sup>7</sup> Further experiments are planned.

B. Activity of Nicotine

It was concluded that nicotine was inactive in this assay based on the absence of a clear dose-response relationship. Addition of nicotine to 2A1 WSC (low alkaloid Kentucky reference) was found to have no effect on WSC activity.

C. Denitrated RL WSC Activities

Tests are in progress on the RL WSCs described above (1. B.). In the first experiment, no unusual features or differences were observed on the dose-response curves of any of the nine WSCs.

3. L5178Y THYMIDINE KINASE (TK) MUTATION ASSAY

Evaluation of TK<sup>-/-</sup> Mutants<sup>8</sup>

The TK enzyme assays were completed on a series of twelve suspected TK<sup>-/-</sup> mutants (induced spontaneously, with positive control

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compounds, or with WSCs) selected in the presence of trifluorothymidine. All of the mutants were found to be deficient in TK activity. The objective of these studies has now been accomplished: to place the assay on a firm molecular basis by confirming that the mutants obtained are truly TK<sup>-/-</sup> based on selective growth and toxicity studies and measurements of TK activity. A Special Report will be written to document these conclusions.

B. Standard versus Modified Cloning Procedure<sup>9</sup>

As alluded to last month, higher spontaneous background and positive control compound activities recently observed have been a cause of concern.<sup>6</sup> The results of an experiment conducted to investigate several possible reasons for the higher responses showed that they were not attributable to: the microsomes; the positive control compounds; or the solvent. Further experiments are planned.

C. Filler Precursors of WSC Activity--LTF Variants<sup>10</sup>

Experiments are in progress to confirm our previous observations regarding the removal of LTF-IIIA filler components.<sup>6</sup> Included in these studies is a comparison of LTF-IIMF *versus* LTF-IIJF, which differ because the latter filler contains urea and color.

4. BHK CELL TRANSFORMATION<sup>11</sup>

The evaluation of our first cell clone was begun by measuring its response(s) to a positive control compound (ethylmethanesulfonate) in growth media containing different types of sera. No transformation was observed under any of the conditions tested. It was observed, however, that freezing the sera (rather than storing them in the refrigerator) led to more reproducible cell generation times in successive passages. Evaluation of a second cell clone is in progress.

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CHARGE NUMBER: 6908  
PROGRAM TITLE: SMOKE CONDENSATE STUDIES  
PERIOD COVERED: April 1-30, 1980  
PROJECT LEADER: R. N. Ferguson  
DATE OF REPORT: May 12, 1980

A. CONDENSATE STUDIES<sup>1</sup>

A sidestream smoke chamber in use by R. Morgan and E. Oakley has been modified so that the sidestream can be trapped on a buffer wetted preptube® cartridge. This should allow development of a method for sidestream nitrosamines. It also appears that sidestream can be bubbled through DMSO for trapping of whole smoke (WS) for subsequent *in vitro* testing. At present, we are only working with 2R1 cigarettes in a static burn mode.

B. NITROSAMINES<sup>2</sup>

A stainless steel heating block for the transfer line from the gc to the tea was fabricated and is working well. We are now obtaining good peak shapes and calibration curves for the major tobacco specific nitrosamine, N-nitroso nornicotine (NNN). However, we have encountered difficulties with NNK [4-N-methyl-N-nitrosamino)-1-(3-pyridyl)-1-butanone] analysis which have not yet been resolved.

The first problem with NNK analysis is the selection of appropriate gas chromatography parameters. The NNK requires temperatures in excess of 250° for elution as a sharp symmetrical peak on the columns tried so far. These conditions sacrifice any separation of the individual tobacco specific nitrosamines. The second problem is that cleanup conditions which provide good recovery of NNN from WSC result in loss of most of the NNK in the sample. We are now attempting to resolve both these problems.

C. MW 288

A study is being conducted to determine if the thermal decomposition of duvatrienediol does lead to formation of one or more MW 288 isomers.<sup>3</sup> This work is based on our earlier findings that duvatrienediols sprayed on filler increase MW 288 found in smoke and the observation that duvatrienediol readily dehydrates under conditions used to obtain a probe mass spectrum to give a ms essentially indistinguishable from that of MW 288 itself. To date, it has been found that at an injection port temperature of 270° (Bendix 2200) there is considerable decomposition of  $\alpha$ -4,8,13-duvatrien-1,3-diol. The decomposition

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products were trapped and analyzed by gc (PE900; 3% OV-22 15' x 1/8" ss column). Retention time data suggest that both major MW 288 isomers seen in smoke are formed by decomposition of  $\alpha$  duvatrienediol at 270°. To complete this study we will apply reversed phase recycle hplc to isolate each of the decomposition products. In the initial run, insufficient material was isolated for  $^1\text{H}$  nmr, so the study will be repeated with a larger sample of duvatrienediol.

To support this work and in preparation for completion of the MW 288 project, all mass spectral data from samples containing MW 288 were compiled.<sup>4,5</sup> As expected the results suggest there are at least two isomers. One isomer appears to lose water to yield an ion at m/e 270. The literature relevant to the geometric configuration of ketones and loss of  $\text{H}_2\text{O}$  under chemical ionization condition was also reviewed.

#### D. CHROMATOGRAPHY

The Sigma 3 gc was converted to a Sigma 3B. The injection port temperature and the detector temperature can now be set independently. We also now have on-column injection capability for the Sigma 3B after installation of a 6' glass  $\mu$  Partisorb (OV17 column). Using methyl stearate, the column provides an efficiency of 900 plates/ft. Emphasis will now be placed on evaluating this column in a gc/ms mode.<sup>4,5</sup>

After considerable discussion and comparative evaluation a memo was prepared recommending the purchase of a HP 5880A capillary gc system. This should facilitate our planned pattern recognition studies on WSC and fractions.<sup>6,7</sup>

Quinoline determinations have now been completed on several samples, but there is still an occasional unexplained problem with this procedure. The latest occurred with RL reference (X6D5AKZ) where recoveries were so low that quinoline could not be quantitated. Although the cause of the problem is unknown, we hope to get usable data after repeating the analysis of this sample.<sup>8</sup>

#### E. BASE FRACTION STUDIES<sup>9</sup> (with 6906)

A more careful study of the high activity fractions from the second LH-20 chromatography of X6D3IM bases was conducted to establish the presence of 2-amino- $\alpha$ -carboline (MW 183). The appropriate fractions were located by analytical reversed phase lc. Several preparative lc analyses provided adequate amounts of MW 183 and a second component (MW 211) for further structural study.

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A  $^1\text{H}$  nmr confirmed that MW 183 was indeed identical to our synthetic sample. This is the first compound of this class which we have definitely identified in WSC. The second unknown has not yet been identified, but a high resolution ms indicated molecular formula of  $\text{C}_{12}\text{H}_9\text{N}_3\text{O}$ . The  $^1\text{H}$  nmr data suggests a carboline type ring system, but further data are needed.

On more than one occasion higher activity has been seen in reversed phase column "strippings" than in earlier eluting fractions. This phenomenon is under more systematic evaluation by study of solvent eluates and "strippings" from several high activity fractions.

F. PYROLYSIS<sup>1,10</sup> (with 6906)

The Mellen furnace was set up so that nitrogen (one liter/min.) was swept through a bed of filler (5 g) heated to 200° then stepped to 250°. The samples used, a control and control plus additive, produced considerable material in the traps. The tobacco, after heating, was much darker but not like a char as seen at higher temperatures. Even at 2 mg/pla activity could not be demonstrated in the *Salmonella*/microsomes assay (TA98 or TA100; with or without S9). The pyrolysis glassware and traps have been completely redesigned and this experiment will be repeated with addition of a higher temperature (300°) step.

G. CARBONYLS IN WSC<sup>11</sup>

This project is essentially complete and a draft Special Report describing the study has been prepared. In checking recoveries in this procedure, it was noted that acrolein forms its 2,4-DNPH in only 22% yield. A later eluting component is however also obtained. This material has now been isolated and has a molecular weight of 236, identical to acrolein 2,4-DNPH but has a different fragmentation pattern. The compound was isolated and a  $^1\text{H}$ nmr gave some support for a postulated structure, 1-[2,4-dinitrophenyl]-2-pyrazoline. Further work will be required to prove this proposal but this will be delayed for studies with a higher priority.

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